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Dynamics of diffusion-controlled recombination of ions in ionic solutions. Limits of validity of the Debye - Smoluchowski equation

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ABSTRACT

The diffusion and recombination process in an ensemble of isolated single pairs of opposite charges is usually described by the Debye - Smoluchowski equation. The present work is an overview of a series of computer simulations of diffusion and recombination of ions in solution performed with the aim to determine the limits of validity of the Debye - Smoluchowski equation.

In the first part of the project, the calculations were performed for the media with the short mean free path (MFP) of the free movement of ions between scattering events, *i.e.*, for the conditions of the diffusion model of the ion transport. Results were obtained on the probability of ion survival as a function of time and the probability of ion escape from recombination at infinite time. The recombination processes in the clusters of non-separable ion pairs and the bulk recombination of ions in solution were simulated. The deviations of the multi-pair kinetics and escape probability from the corresponding results of the calculations performed on a basis of the Debye-Smoluchowski theory are significant but we found that the Debye-Smoluchowski recombination rate constant can be applied for all concentrations of ions.

We also consider the effects of restricted geometry and anisotropy of the medium on the kinetics of the recombination of oppositely charged species in each other's field and the escape probability. This model roughly corresponds to the electron - cation recombination in organic crystals.

The results for short MFP's were then compared with the results of the calculations of the electron - cation recombination in the systems characterized by long MFP of electron between the scattering events. It was found that for long mean free paths, above 10-20 % of Onsager distance in the medium ($R_c = e^2 / 4\pi\epsilon\epsilon_0 kT$, $\epsilon\epsilon_0$ is the dielectric permittivity of the medium, e - electron charge, $k_B T$ - the thermal energy), the recombination theory based on the Debye - Smoluchowski equation is no longer valid, even for isolated ion pairs.

Keywords: diffusion, ion recombination, rate constant, ionic solutions, computer simulation.

1. INTRODUCTION

The present theoretical basis for diffusion-controlled recombination of ions is provided by the Debye - Smoluchowski (DS) equation^{2,3} (see¹ for a source of references)

$$\partial C / \partial t = \nabla \{ D [\nabla C + (C / k_B T) \nabla U] \} \quad (1)$$

where $C(r, t)$ denotes the density of ions as a function of their spatial coordinates and time, V is the interaction potential between ions, D is the sum of the diffusion coefficients of cations and anions, k_B and T - the Boltzmann constant and temperature, respectively.

Unfortunately, this equation describes in fact only a single pair of interacting particles in space. If the interaction potential V corresponds to the Coulomb interaction $-e^2/4\pi r\epsilon\epsilon_0$ in a dielectric continuum with the permittivity $\epsilon\epsilon_0$, then we can write the specific version of the equation for ions. In radial coordinates we obtain

$$\partial C/\partial t = D\{\partial^2 C/\partial r^2 + (2/r + R_c/r^2) \partial C/\partial r\} \quad (2)$$

with the boundary conditions at the encounter radius R in the form of either

$$C(R,t) = 0 \quad \text{or} \quad (3)$$

$$k_R C(R,t) = 4\pi R^2 D (\partial C/\partial r) \big|_{r=R} \quad (4)$$

where the former is known as the Smoluchowski condition and the latter as the radiation boundary condition, with k_R the reaction rate at encounter. The parameter R_c is called the Onsager radius and is defined as the distance at which the energy of the Coulomb interaction in dielectric continuum becomes equal to the thermal energy $k_B T$:

$$R_c = e^2/4\pi\epsilon\epsilon_0 k_B T \quad (5)$$

The DS equation looks deceptively simple. Its approximate solutions are known already quite long time (see ¹ for a review) but the full state-of-art solution for $C(r,t)$ has been published by Hong and Noolandi ⁴. When the spatial variable from $C(r,t)$ is integrated out, we obtain $P(t)$, the survival probability of an ion pair as a function of time. Proper averaging of $P(t)$ over the initial spatial arrangements of charged species leads to a time dependent quantity that can be compared with the macroscopic recombination kinetics. The limiting value of the spatial integral of $C(r,t)$, at infinite time, represents the probability that an ion escapes recombination and is known as the ion escape probability. The (simplified) formula given by Onsager ^{1,4} is as follows

$$P_{esc} = \{ \exp(-R_c/R_0) - \exp(-R_c/R) \} / \{ 1 - \exp(-R_c/R) \} \approx \exp(-R_c/R_0) \quad (6)$$

where R_0 is the initial distance between the counterions.

The DS equation has been derived for charged species with a short mean free path (MFP) between consecutive collisions with the molecules of an isotropic medium, i.e. for ionic species or for excess electrons with a relatively low mobility. Therefore, incorrect results may be obtained when the DS equation is applied to a physical system for which one or more of these assumptions is violated. In this paper we consider the following major causes of breakdown of the DS equation:

- (1) Presence of multiple ion pairs (which leads to breakdown of the scaling properties of the DS equation);
- (2) Anisotropy of diffusion tensor
- (3) Long mean free paths of mobile charges and velocity-dependent scattering mechanism of mobile charges

The present work is an overview of a series of computer simulations of diffusion and recombination of ions in the systems containing isolated ion pairs or a number of nonseparable ion pairs, the systems with short or long MFP, and the systems with significant anisotropy of diffusion coefficients.

2. COMPUTER SIMULATION METHOD

The method which has been selected for calculations of the diffusion processes belongs to the class of the Stochastic Dynamics methods (Allen and Tildesley ¹²). The method ignores the neutral particles of the medium and treats them as a dielectric continuum - only the ions in the sample are treated on the molecular level. The influence of the neutral molecules is simulated by the random walk of the ions. This method has been successfully used to simulate the ion recombination in the ionization tracks of high-energy particles in nonpolar media ^{6, 7, 13}. This section will be devoted to a more detailed description of the computer simulation programs.

2.1. The diffusion type of transport of charged species (short MFP)

The initial positions of the ions are represented by a set of numbers in the computer memory. Different rules of the ion distribution in the systems can be applied - from fully random distribution of ions, through simulation of the Boltzmann

distribution, to regular geometrical arrangements of the ions. The simulation method does not account for the actual velocity of the ions nor the movement of the neutral molecules of the medium. We assume that the frequency of collisions of an ion with the medium molecules is so high and its mean free path between the collisions is so short that the ion velocity is a random variable. The influence of the medium molecules on a given ion is modelled by the random walk (Brownian movement) of an ion in continuous medium. The random vectors are obtained from the random number generator and they are properly scaled using the Einstein relation - the mean value of the squared distance in the Brownian motion is proportional to the time of motion and the proportionality coefficient is calculated from the experimental diffusion coefficient $\langle(\Delta r)^2\rangle = 6D\Delta t$. The ion drift vectors in electric field are obtained by solving the electrodynamic equations of motion using experimental mobilities of the ions. It is of course possible to include any type of external field affecting the movement of ions.

2.2. The transport of charged species with long MFP

The initial conditions in the long MFP case include also the velocities of the electrons which are sampled from the Maxwell - Boltzmann distribution for an assumed temperature. The random directions of the electron velocities are assumed. The simulation method does not account for the actual velocity of the positive ions nor the movement of the neutral molecules of the medium.

New positions of the cations and electrons are calculated in discrete time steps using the two-timescale technique. The long time step Δt_c is selected for cations. Due to high electron mobility, the position of an electron can change quite significantly during the cation time step. The short time step Δt_e is selected for a given electron in the following procedure. First, an actual value of the electron path λ is sampled from the exponential distribution of λ . Having selected the time step Δt_e , the trajectory of a given electron is calculated by the numerical solution of the electrodynamic equations of motion (for a classical particle). At the end of the trajectory the mobile charge is scattered. The scattering mechanism was based on the assumption of complete randomization of velocity of the electron on collision. The model seems to be oversimplified, particularly in the case of elastic scattering and the correlations. On the other hand, the assumption of the full randomization of the electron momentum makes possible the direct comparisons between the diffusion transport and the long MFP cases and systematic investigation of the recombination kinetics and the escape probability as functions of the MFP length.

For the both cases, short and long MFP, new positions of the ions are calculated in discrete time steps. If any ion pair fulfills the assumed recombination criteria the algorithm simulates the ion recombination - the ions disappear from the file of the "living" ions and their positions are no longer modified. The program records the time from the beginning of the simulation run which will serve to construct the kinetics of the recombination process.

The simulation runs until a prescribed number of time steps (usually 10^4 or 10^5 time steps) or is terminated in the case of disappearance of all the ions in the simulated sample. The program starts again for a new geometrical configuration of ions and is repeated for a large number of the configurations. To obtain a good statistics of the recorded data and smooth kinetic curves, as much as about 10^6 ions are necessary, and even more in certain specific cases like the investigation of the long-time effects.

3.RESULTS AND DISCUSSION

3.1. Recombination in ensembles of clusters of nonseparable ion pairs - short MFP case.

There are numerous examples of multiple ion-pair systems. The ionic solutions which undergo some form of ionic reaction, ion pairing or nucleation make an obvious example. Typical concentrations of ions, from 10^{-4} M to 10 M, cause any reduction of the system to a collection of isolated ion pairs to be rather far from physical reality. Another example of the ensembles of nonseparable ion pairs is provided by the ionizing radiation. A high-energy particle when passing through condensed medium leaves in its wake clusters of ion pairs - 2, 3, 4 or even more ion pairs. In the case of heavy particles, like the α particles, we observe the columns of ionization. The ion pairs can not be separated and treated as the isolated entities. In the study of the chemical effects of high-energy radiation the consideration of the nonhomogeneous spatial distribution of the chemically active transients in the track plays an important role and considerable attention has been given to this problem, notably for the case of water and nonpolar liquids.

The recombination processes in spurs with more than one ion pair were studied by several authors. For the hydrocarbon systems characterized by short free paths of charged species, Bartczak and Hummel^{6,7} proposed a random flight simulation. They found that the multipair effects may lead to substantial changes in the recombination kinetics, the ion escape

probability at infinite time as well as the singlet/triplet ratio among the recombination products^{8,9}. Extensive studies of the multipair effects in different systems were performed by Green and coworkers (see^{10,11} and references therein).

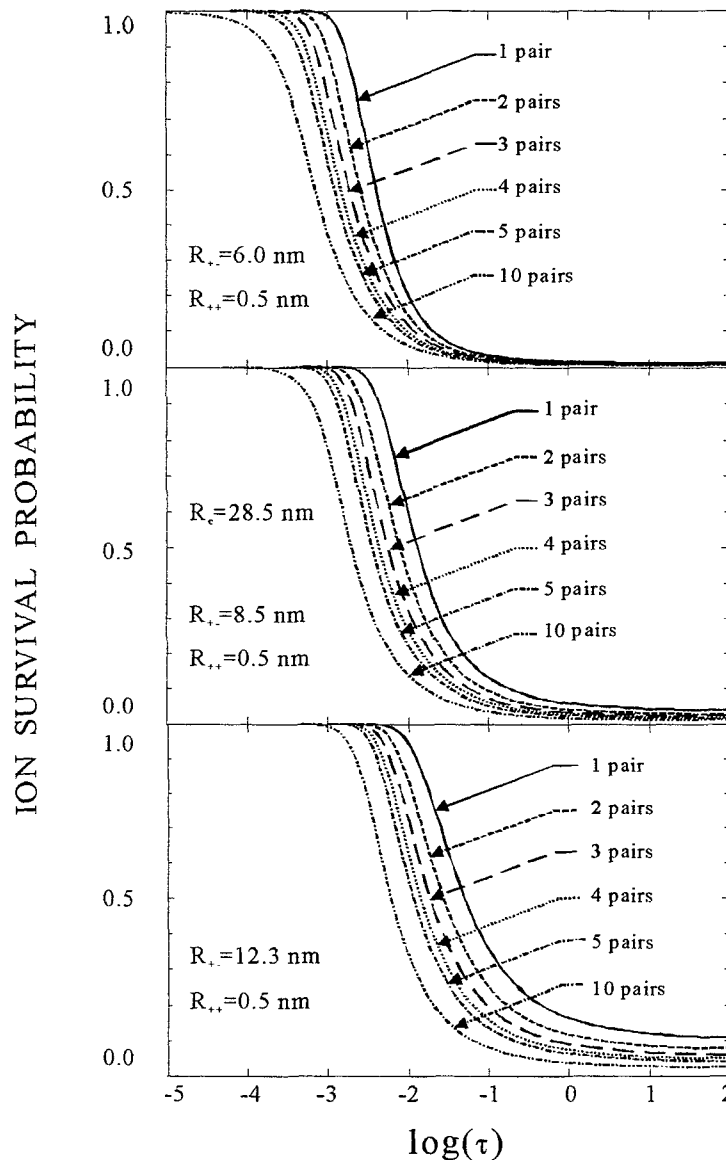


Fig. 1. The ion survival probability as a function of the logarithm of time for single-pair (full curve) and for multi-pair systems. The calculations correspond to the short MFP or diffusion model. The broken curves correspond to clusters initially composed of 2, 3, 4, 5 and 10 ion pairs, respectively. The initial distance between cations of different pairs is $R_{++}=0.5$ nm, the initial distance between cation and anion of the same pair is: $R_{+-}=6.0$ nm (upper figure), $R_{+-}=8.5$ nm (middle part) and $R_{+-}=12.3$ nm (lower figure). The diffusion coefficients for cations and for anions are $D_+ = D_- = 1.26 \times 10^{-9}$ m²/s, the Onsager radius is $R_c=28.5$ nm, the reaction radius $R=1.0$ nm. The time is expressed as a dimensionless parameter $\tau=Dt/R_c$.

The simulation of the ion recombination processes has been performed for systems of isolated clusters of ions, containing 1, 2, 3, 4, 5 and 10 nonseparable ion pairs^{6,7} (later it was extended to large systems, such as ionization tracks¹³). An example of the results of the simulation, in the form of the time evolution of the ion survival probability, is given in Figure 1. The calculations allow us to compare the recombination kinetics calculated for the single pairs (the solution of the Debye-Smoluchowski equation) with those calculated for the multiple-pair clusters. The initial distance between the cation and the anion of a pair is assumed as $R_{+-}=6.0$ nm, 8.5 nm and 12.3 nm for the upper, middle and lower part of the figure, respectively. In the case of the clusters composed of more than one ion pair, the cations are placed on a straight line, $R_{++}=0.5$ nm apart, and the anion from a given pair is selected in random direction around its geminate cation. We performed the test calculations for different geometrical arrangements of the cations and the results were very similar. The calculations correspond to the ions in a nonpolar medium, with the dielectric permittivity $\epsilon=2$ and the Onsager radius $R_c=28.5$ nm.

The figure proves that the multiple-pair effects in the diffusion equation are indeed significant. The full line on the right hand side of the series of the kinetic curves represents the single-pair solution of the DS equation. One can see that even the recombination of ions in two-pair clusters shows some deviations from the single-pair model. When we refer to the kinetics obtained for the 10-pair clusters, the kinetics of the process is shifted by a time decade (the abscissa is expressed in the logarithmic scale) with respect to the DS kinetics.

Figure 2 shows the dependence of the ion escape probability on the initial cation - anion distance for single pairs (full line calculated from the Onsager formula) and for the clusters of 2, 3, 4, 5 and 10 ion pairs. The abscissa is defined as the inverse distance $1/R_{+-}$, the scale of the ordinate is logarithmic. In this coordinate system the Onsager dependence is linear. The dashed and dotted curves represent the best fitting to the results for 2,3,4,5 pairs. For these clusters, the curvature of the fitted curves is very slight. The fitting for the 10-pair clusters shows more significant deviation from linearity. The ion escape probability for the clusters of more than one ion pair is lower than the Onsager probability. It is important to underline that this rule is true only for short distance between the cations, $R_{++}=0.5$ nm, for which the calculations of Fig. 2 have been performed.

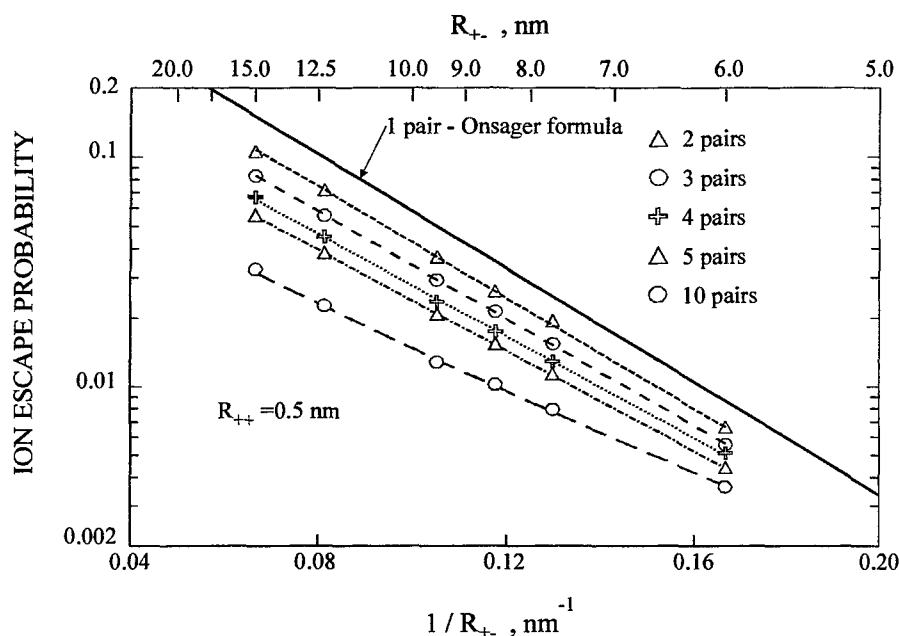


Fig. 2. The P_{esc} for the diffusion model as a function of the initial cation-anion distance for ions in groups of 2, 3, 4, 5 and 10 ion pairs with the separation of $R_{++}=0.5$ nm between cations and for single pairs (full line, calculated from the Onsager formula). The parameters are: the reaction radius $R=1.0$ nm, $R_c=28.5$ nm. The distance R_{+-} is given as the upper abscissa, $1/R_{+-}$ is given as the lower abscissa.

Interesting example which shows the potential of the simulation method in analysis of ion diffusion process is given below. Two important scaling properties of the DS equation can be mentioned: i) the time evolution of the ion density and its spatial integral, *i.e.* the ion survival probability, depends on the sum of the diffusion coefficients $D_+ + D_-$ but does not depend on the individual coefficients; ii) the probability P_{esc} that an ion escapes recombination after infinite time does not depend on the diffusion coefficients of the cations and anions at all.

Using the computer simulation method we calculated the ion survival and the ion escape probability as a function of time in the systems composed of independent clusters of pairs, from $N=1$ to 10 pairs. The sum of the diffusion coefficients is, for all the simulations, $D_+ + D_- = 2D = 2.528 \times 10^{-9} \text{ m}^2/\text{s}$. The calculation of the ion escape probability as a function of N was performed for three cases: for immobile anions $D_-=0$ and mobile cations, for the same mobilities of cations and anions $D_+=D_-=D$ and for immobile cations $D_+=0$. The recombination kinetics is different for these cases, in contrast with the first scaling property of the DS equation. We observe quite significant difference between the extremal cases of the escape probability P_{esc} : $D_+=0$, and $D_-=0$. The ions in the $D_+=2D$ case recombine faster at the initial phase of the process but the ion decay slows down at long times and its asymptotics, *i.e.* the escape probability, is higher than the $D_+=0$ result.

3.3. Kinetics and rate constant of bulk recombination of ions in solutions

It is assumed (ref.¹, p.59) that for high ionic concentrations the rate of recombination decreases below the Debye-Smoluchowski limiting rate

$$k_{DS} = 4\pi R_c D / \{1 - \exp(-R_c/R)\} \approx 4\pi R_c D \quad (7)$$

towards the rate typical for neutral molecules:

$$k_s = 4\pi R D. \quad (8)$$

The conjecture is reasoned out as follows. In the system of many ionic charges, the charges of an individual pair are in a sense neutralized. When two ions are alone in space the Coulomb field dominates the diffusion processes but in the system of a large number of charges the ions should behave like almost neutral molecules and their effective radius of influence is reduced from a large Onsager radius R_c to a much smaller radius comparable with the encounter radius R . In the case of hydrocarbons we can expect quite substantial reduction of the rate constant at high concentrations (by a factor of 100). For polar solutions the reduction of the rate constant is not so spectacular, but even in the case of aqueous solutions we can expect the reduction by a factor of 2-3.

The recombination kinetics described so far is calculated for the multiple-pair but finite systems. In order to simulate infinite systems the periodic boundary conditions have been introduced. We place a certain number of ions in the simulation box. If we assume a given size of the box then the number of ions is calculated from the concentration. The central box is then repeated periodically in all three directions: x , y , z . The typical size of the box differs from 10 nm to 20 nm and usually contains few hundred independent ions. The infinite size of the system causes also another problem. The Coulomb forces are of infinite range and the ions from even very far boxes interact with the ions from the central box. Therefore the field acting on a given ion has to be calculated by summing up the contributions from infinite number of ions. The Ewald method has been used to calculate these forces in our simulations. The method is explained in the Allen and Tildesley book¹².

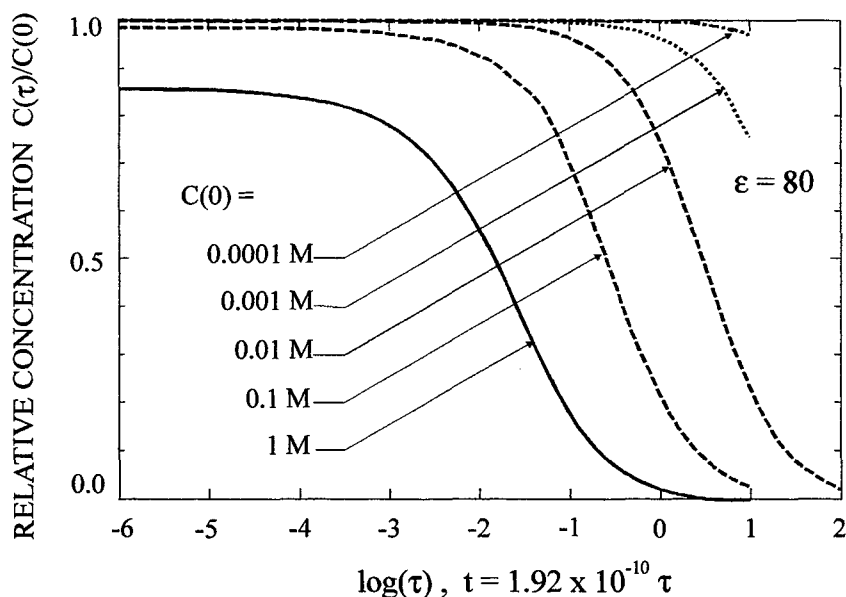


Fig. 3. The ion survival probability as a function of the logarithm of the dimensionless time τ obtained by the computer simulation of the diffusion and recombination of ions in solutions with the dielectric constant $\epsilon=80$ and for the ion concentrations 10^{-4} M, 10^{-3} M, 10^{-2} M, 10^{-1} M, 1 M.

Figure 3 shows the evolution of the relative concentration of ions for the ion recombination in ionic solutions, for a series of initial concentrations: 10^{-4} M, 10^{-3} M, 10^{-2} M, 10^{-1} M, 1 M. The simulation was performed for the dielectric constant $\epsilon=80$, which corresponds to an aqueous solution. The figure shows the recombination kinetics as a function of the dimensionless time τ , which is defined as $\tau=Dt/R_c^2$ and, for the assumed parameters, we have the relation between the real time and the dimensionless time that is given in the figure. The time axis is expressed as the logarithmic scale. The time scale spans over eight time decades.

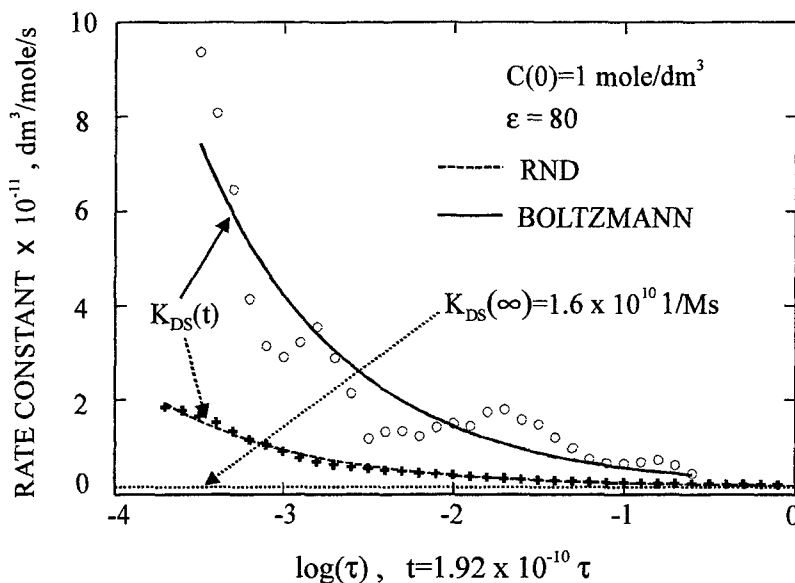


Fig. 4. The results of the rate coefficient calculations for the ion concentration $C=1$ M in an aqueous solution ($\epsilon=80$).

The circles and crosses show the rate coefficient of recombination as a function of the logarithm of (dimensionless) time calculated by direct differentiation of the simulated kinetics of Fig. 3. The circles correspond to the Boltzmann initial distribution of cation – anion distances, the crosses correspond to a random configuration of ions. The full and dashed curve show the time dependence rate that results from the Debye-Smoluchowski model for the Boltzmann and random condition, respectively, and the dotted horizontal line is the stationary rate constant.

The reaction rate constant has been calculated by direct differentiation of the ion survival probability $P(\tau)$ over the time τ . The results of the rate constant calculation are given in Figure 4. These results show the time dependence of the rate constant. The cricles show the simulated rate coefficient for the Boltzmann initial distribution of the cation – anion distances and the crosses for the random configuration of ions. The Debye-Smoluchowski rate constant (calculated from the full time - dependent formula) is shown also in the figure as the full line for the Boltzmann condition and the dashed curve for the random condition. The asymptotic value of the rate is $k_{DS} = 1.614 \times 10^{10}$ l/mole/s, more than two times higher than the rate for neutral molecules $k_S = 4\pi RD = 0.747 \times 10^{10}$ l/mole/s (the encounter reaction radius has been assumed as 0.4 nm). The simulated rate reaches the steady state value in the last decade. The rate is 2.05×10^{10} l/mole/s.

Figures 5 and 6 summarize the results of the rate constant calculations. In Figure 5 the rate constants are shown as a function of the initial concentration of ions in the solution, $C(0)$. Two sets of the rate constants are given: for $\epsilon=10$ and $\epsilon=80$. The corresponding horizontal lines show the values of the steady-state Debye-Smoluchowski rate constant. In Figure 6 the rate constants are given as function of the dielectric permittivity of the solution ϵ . The simulated results (squares) for $C(0)=0.01$ M, for which the interionic distance is on average about 4.4 nm, are compared with the theoretical Debye-Smoluchowski rates (full curve) and with the rate for the neutral molecules (horizontal dotted line).

Commenting upon the results of these calculations, we found rather interesting and unexpected behaviour of the diffusion-controlled recombination processes in concentrated ionic systems. According to qualitative conjectures, it was expected that the rate constant will decrease with the increase of the ion concentration, from the Debye-Smoluchowski limiting rate for the isolated pairs to the rate constant $k_S=4\pi RD$ typical for neutral molecules (represented in Figures 5 and 6 by the horizontal dashed line). However, the picture obtained from the simulations is different. Roughly, we can summarize it as follows: the ions of the reacting ion pair are not influenced by all the other charges of the system and their reaction rate does not depend on the overall density of charge. The discussion of these results from the point of view of experimental measurements of the rate constant of ionic reactions is given in ^{17, 19}. Marciniak and Rozwadowski ¹⁸ investigated the reaction rate constants for the recombination of the positively charged organic ions (derivatives of pyridine) with a series of singly and multiply charged ions with the concentration of between 10^{-3} and 10^{-2} mole/l. They obtained the rate constants about 1.3×10^{10} l/mol/s whereas the rate constants for similar reactions but with neutral molecules were about 4×10^9 l/mol/s, more than 3 times lower. These results are in very good agreement with our simulation results.

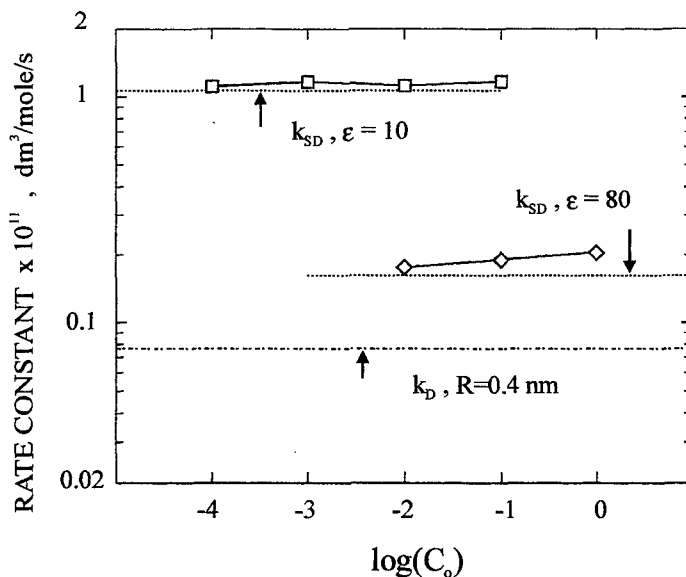


Fig 5. The compilation of the rate constants from the simulations of the homogeneous recombination. The steady state rate constant is given as a function of the initial ion concentration in the solution. The squares show the results for slightly polar solutions ($\epsilon=10$), the diamonds correspond to aqueous solutions ($\epsilon=80$). The horizontal dotted lines in the vicinity of the simulated rate constants show the values of the theoretical, single-pair rate k_{DS} . The dashed line at the bottom of the figure shows the value of the rate constant for the neutral particles reacting at encounter.

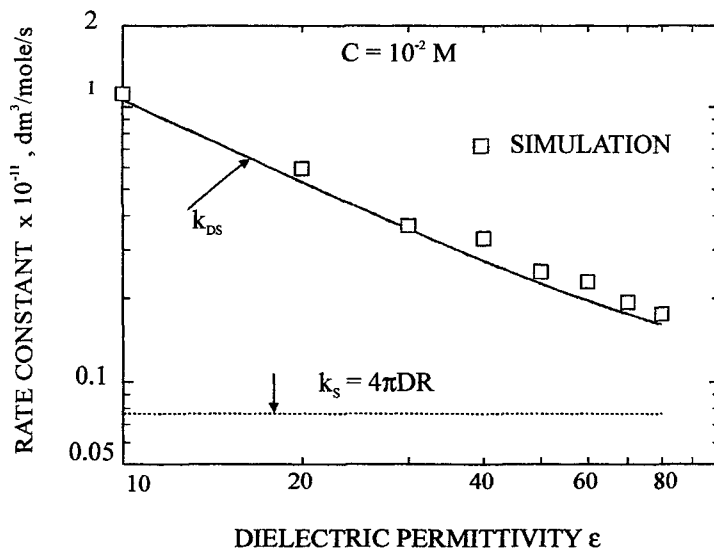


Fig 6. The rate constant of the ion recombination in the solutions with the initial concentration $C(0)=10^{-2}$ M calculated as a function of the dielectric permittivity of the solution. The results of the simulation are shown as the squares, the single-pair Debye-Smoluchowski rate constant is shown as the full curve, the rate constant for neutral molecules with $R=0.4$ nm is represented by the horizontal dotted line.

3.4. The charge recombination in the systems characterized by anisotropy of diffusion coefficient

Studies of the migration of the charged species induced by high-energy radiation in various solid systems have been carried out recently¹⁵. In some cases the kinetics of the charge recombination is complicated by the fact that the mobility of the charged species differs in different directions. For example, in crystalline polyethylene a large anisotropy has been observed, the mobility having been found to be at least a factor of 100 larger in the direction of the chain than perpendicular to it¹⁶. In various "conducting" polymers the charge migration takes place along the chain and in phthalocyanine and porphyrin aggregates along the columnar stacks.

For the computer experiments discussed in this chapter¹⁴ we assume that the medium is characterized by the diffusion coefficient D_z in the z -direction and the diffusion coefficient $D_x=D_y=D$ in the direction perpendicular to the z -axis. The degree of anisotropy is represented by the coefficient $\delta=D_z/D$. The diffusion tensor is thus assumed in the diagonal form, without any off-diagonal components. The diagonal elements D_z and $D_x=D_y$ can differ as much as by factor of 10 in our calculations, although in molecular crystals the ratio δ does not exceed the value of 2-3. In the present calculations we assume δ as a free parameter and we perform the simulations for selected values of δ from the range 1 - 10. When the calculations have to be compared with the isotropic case, we calculate the effective diffusion coefficient, D_{eff} , defined as the cube root of the determinant of the diffusion tensor, $D_{eff}=D(\delta)^{1/3}$.

Figure 7 shows the kinetics of the ion recombination. The probability of the ion survival against recombination up to time t is plotted as a function of the logarithm of the dimensionless time $\tau=Dt/R_c^2$, $D=D_{eff+}+D_{eff-}$, and D_{eff} is the cube root of the determinant of the respective diffusion tensor. The kinetics in Fig. 8 were calculated for relatively high anisotropy coefficient $\delta=10$. Different curves in the figure correspond to different angles θ between the z -axis (*i.e.* the direction of the fast movement) and the axis defined by the cation and anion of the pair. The calculations were performed for the angles: 0° (the pair axis aligned with the z -axis), 30° , 60° , 90° (the pair axis perpendicular to the direction of the fast movement). These calculations are represented by the broken or dotted curves. The thick full line gives the results of the calculations for the averaged kinetics: the negative ion was produced on a sphere in a random direction around the positive ion. In all the cases the initial cation - anion distance was fixed: the initial distance was $R_{+-}=7.7$ nm. Finally, the thin continuous curve shows the corresponding kinetics in isotropic media. The diffusion coefficients are: for cations $D_{+z}=\delta D_+$, $D_{+x}=D_+$, $D_{+y}=D_+=2.527 \times 10^{-10}$ m²/s, for anions $D_{-z}=\delta D_-$, $D_{-x}=D_-$, $D_{-y}=D_-=2.527 \times 10^{-8}$ m²/s. The medium parameters correspond to a nonpolar medium with the Onsager radius $R_c=30$ nm.

The recombination kinetics for different angles θ are significantly different one from another even for low anisotropy. For the anisotropy coefficient $\delta=10$ the curves for $\theta=0^\circ$ and $\theta=90^\circ$ are shifted by more than a time decade. The recombination at low angles θ is the fastest and the escape probability is the lowest. In the contrary, for high θ the recombination process is slower and the escape probability very high. For $\delta=2$ the escape probability at $\theta=90^\circ$ is almost 4 times higher than the probability at $\theta=0^\circ$, for $\delta=10$ the ratio of the escape probabilities can be as high as 30 - 40. The angle averaged kinetics of recombination has no longer typical shape of the diffusion-controlled kinetics but extends over large number of time decades and becomes similar to the dispersion-type kinetics with time-dependent rate constant.

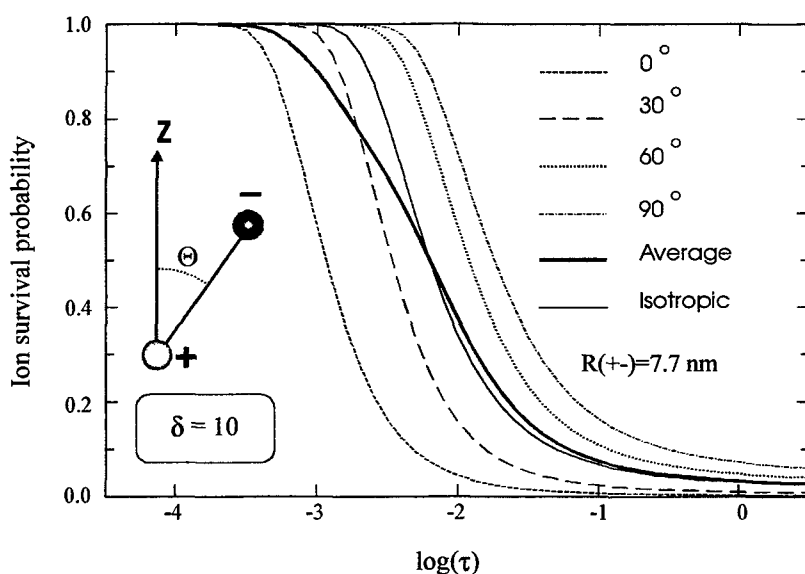


Fig. 7. The ion survival probability as a function of logarithm of (dimensionless) time for the systems with axial anisotropy. The anisotropy coefficient $\delta=10$. The series of broken curves correspond to the following angles θ between the z -axis of the coordinate system and the position vector of the anion relative to the position of the cation of a pair: $\theta=0^\circ$, 30° , 60° and 90° . The thick continuous line shows the kinetics averaged over the angle θ , the thin line is the isotropic kinetics.

3.5. Kinetics and escape probability for different lengths of MFP - recombination of isolated ion pairs.

Electron mobility μ in chain or cyclic hydrocarbons is low: in *n*-pentane and *n*-hexane at room temperatures is $1.4 \times 10^{-5} \text{ m}^2/\text{Vs}$ and $0.9 \times 10^{-5} \text{ m}^2/\text{Vs}$, respectively, in cyclohexane $3.5 \times 10^{-5} \text{ m}^2/\text{Vs}$ (see for instance ⁵). There is however a class of liquids where an excess electron has much higher mobility: tetramethylsilane ($\mu=1 \times 10^{-2} \text{ m}^2/\text{Vs}$ at 296 K), methane ($\mu=3.73 \times 10^{-2} \text{ m}^2/\text{Vs}$ at 120 K), argon ($\mu=4.9 \times 10^{-2} \text{ m}^2/\text{Vs}$ at 87 K), etc. Using Langevin relation (see ref. ⁵) between the electron MFP λ and the mobility μ : $\mu = \lambda (e/3k_B T) U_{rms}$ (where U_{rms} is the root mean square velocity of thermalized electron calculated from the Maxwellian distribution) we obtain the MFP for electron in *n*-pentane or *n*-hexane of the order of $1 \times 10^{-2} \text{ nm}$ but in tetramethylsilane the MFP is 6.05 nm, in methane 22.5 nm and in argon 29.6 nm. The latter MFP's are similar to the Onsager distance in these media.

In the case of a large MFP the electron may pass, keeping to an orbital trajectory, at a very short distance from a positive ion, without recombining, and move away from the cation again. Experimental evidence for this phenomenon is given by the decrease of the recombination rate k_r for high mobility systems, e.g. liquid methane. Also the increase of the yield of escaped charges in such systems as liquid methane, neopentane and tetramethylsilane in comparison with low mobility liquids may be an indication of this phenomenon. An excellent review of the experimental and theoretical results on ion recombination in the systems characterized by long mean free path of electrons is given by Schmidt ⁵. The calculations (see refs. ^{5,20}, for a source of references) have proven that when the MFP of electrons is increasing towards the values of the order of the Onsager length R_c in a given medium, the theory of transport and recombination of charges that is based on the DS equation does not describe properly the recombination kinetics, ion escape probabilities nor rate constant of recombination. In the case of the geminate recombination, the escape probability at infinite time becomes higher than the probability that results from the Onsager formula, much higher for MFP of the order of R_c . The rate constant for electron - cation recombination in high-mobility liquids k_r is lower than the DS rate $k_{DS}=4\pi D R_c$. There is no explicit calculation of the electron - cation geminate recombination process in the system of more than one e^- -cation pair. This is particularly important in the experiments where the electron - cation pairs were produced by ionizing radiation and a large part of the ionization appears in the form of clusters of nonseparable ion pairs.

In order to compare the results for long MFP with the calculations performed for short MFP and low mobility electrons, the first series of the simulations has been performed for single pairs electron - cation. The results of the calculations of the kinetics of recombination are presented in Figure 8. The kinetic curves are plotted versus logarithm of the dimensionless time τ defined as $\tau=Dt/R_c^2$ where $D=e\mu/k_B T$ is the diffusion coefficient of the electrons (the diffusion coefficient of the cations is negligible as compared to D).

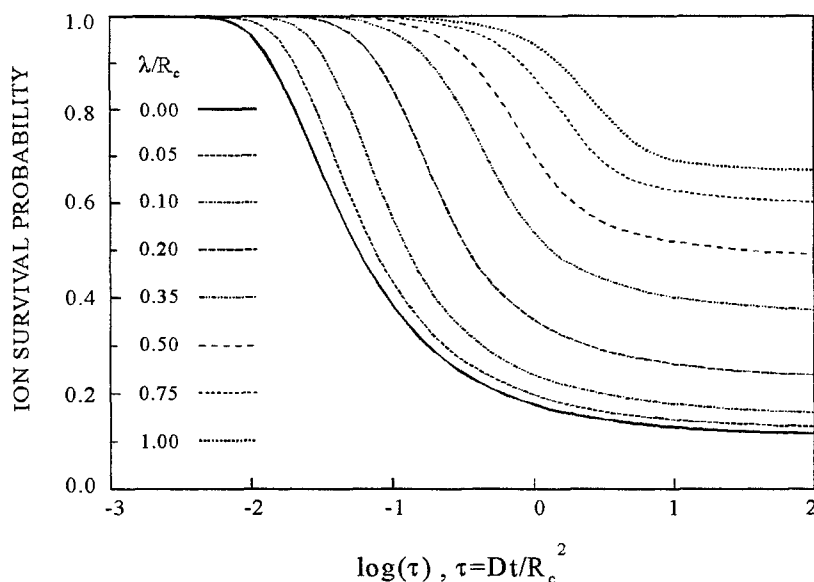


Fig. 8. The probability of electron survival up to the time t plotted as a function of the logarithm of $\tau=Dt/R_c^2$. The calculations were performed for single ion pairs. The different curves correspond to different length of the mean free paths (MFP) of electron: from $\lambda=0$ (the infinitely short MFP or the DS case), for $\lambda=0.05R_c$, $0.10R_c$, $0.20R_c$, $0.35R_c$, $0.50R_c$, $0.75R_c$ to $\lambda=1.0R_c$, where $R_c=28.5 \text{ nm}$ is the Onsager radius. The cation - electron initial distance is $R_+=0.45R_c$.

The full curve is calculated on a basis of the diffusion model and represents the DS kinetics of the ion recombination for isolated ion pairs in a nonpolar medium with $R_c=28.5$ nm. Physically, this kinetics corresponds to the electrons with mobility of the order of $5 \times 10^{-8} \text{ m}^2/\text{Vs}$, i.e. the mobility of the classical ions. The remaining kinetic curves correspond to the mean free path of the electrons of $0.05R_c$, $0.10R_c$, $0.20R_c$, $0.35R_c$, $0.50R_c$, $0.75R_c$ and $1.00R_c$ or to the electron mobilities from $2.4 \times 10^{-3} \text{ m}^2/\text{Vs}$ to $4.7 \times 10^{-2} \text{ m}^2/\text{Vs}$ for $0.05R_c$ and $1.00R_c$, respectively. It is worth to note a dramatic difference between the DS kinetics and the kinetics for the MFP $\lambda=1.00R_c=28.5$ nm. The results for the MFP $\lambda=0.20R_c$ are also very much different from the diffusion-controlled limiting case. The DS kinetics may be, with acceptable errors, applied only to the case of $\lambda=0.05R_c=1.43$ nm and this seems to be the limit of applicability of the DS equation.

Figure 9 shows the results of the calculations of the probability that an electron - cation pair ultimately escapes recombination. The probability is plotted as a function of the initial cation - electron separation R_+ . The results were obtained from the long-time parts of the kinetic curves by fitting the kinetics to the function τ^α and taking the limit $\tau \rightarrow \infty$. A series of calculations were performed for the following values of the MFP λ : $0.05R_c$, $0.10R_c$, $0.20R_c$, $0.35R_c$, $0.50R_c$, $0.75R_c$, $1.00R_c$, labeled in the figure. The curve marked with "+" and the label ONS was calculated from the Onsager formula for the diffusion-controlled case: $P_{esc} = \exp(-R_c/R_+)$. Similarly as in the case of the kinetic curves of Figure 1, we can see dramatic differences between the Onsager escape probability and the probability for the MFP $\lambda > 0.05R_c$. The increase of the escape probability above the Onsager limit exceeds an order of magnitude.

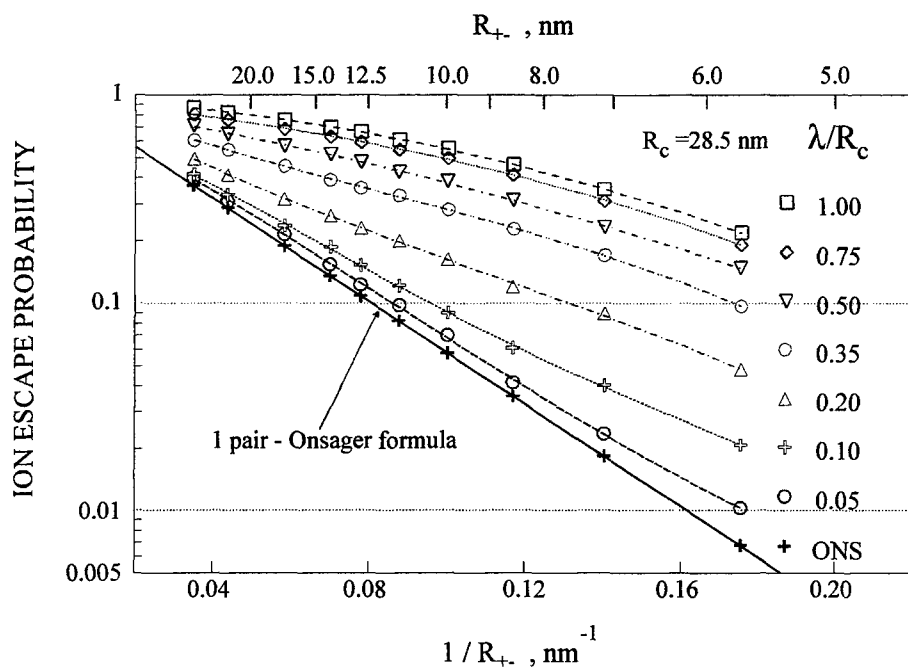


Fig. 9. The escape probability as a function of the inverse of the initial cation - electron distance R_+ . The calculations were performed for single ion pairs. The different curves correspond to different lengths of the mean free paths (MFP) of electron: from $\lambda=0$ (the Onsager case, marked ONS), for $\lambda=0.05R_c$, $0.1R_c$, $0.2R_c$, $0.35R_c$, $0.5R_c$, $0.75R_c$ to $1.R_c$.

4. CONCLUSIONS

The limits of validity of the Debye - Smoluchowski equation applied to diffusion-controlled recombination of charges were investigated by means of the computer simulation method.

The scale of the deviations of the kinetics of the recombination process in the multi-pair clusters from the kinetics for the isolated pairs was estimated. The deviations of the multi-pair kinetics and escape probability from the corresponding single-pair results are significant. The kinetic curve for recombination in multi-pair clusters may be shifted by more than time decade from the DS kinetics and the escape probability can be lower by an order of magnitude than the Onsager probability for the same set of parameters. However, in the case of the bulk recombination of ions in solution, in spite of the significant difference of the simulated kinetics and the DS kinetics, the steady-state rate constants of recombination are quite close to the k_{DS} rate, even for very high concentration of ions.

Some differences between the simulated kinetics and the DS kinetics were also noted for the systems with marked anisotropy of the diffusion tensor.

For the processes with long mean free path of charges the scale of deviations is much higher. If the length of the electron MFP exceeds, say, $0.05R_c$, the deviations of the recombination kinetics and the escape probability from the respective values obtained on a basis of the diffusion mechanism are so large, that neither the DS equation nor the Onsager formula can be applied to describe the recombination between positive and negative charges.

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